Impact of metals in surface matrices from formal and informal electronic-waste recycling around Metro Manila, the Philippines, and intra-Asian comparison

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ABSTRACT

We report concentrations, enrichment factors, and hazard indicators of 11 metals (Ag, As, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, and Zn) in soil and dust surface matrices from formal and informal electronic waste (e-waste) recycling sites around Metro Manila, the Philippines, referring to soil guidelines and previous data from various e-waste recycling sites in Asia. Surface dust from e-waste recycling sites had higher levels of metal contamination than surface soil. Comparison of formal and informal e-waste recycling sites (hereafter, "formal" and "informal") revealed differences in specific contaminants. Formal dust contained a mixture of serious pollutant metals (Ni, Cu, Pb, and Zn) and Cd (polluted modestly), quite high enrichment metals (Ag and In), and crust-derived metals (As, Co, Fe, and Mn). For informal soil, concentration levels of specific metals (Cd, Co, Cu, Mn, Ni, Pb, and Zn) were similar among Asian recycling sites. Formal dust had significantly higher hazardous risk than the other matrices ($p < 0.005$), excluding informal dust ($p = 0.059$, almost significant difference). Thus, workers exposed to formal dust should protect themselves from hazardous toxic metals (Pb and Cu). There is also a high health risk for children ingesting surface matrices from informal e-waste recycling sites.

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1. Introduction

Electronic-waste (e-waste) recycling in developing countries is a source of toxic metals that can spread to local environments. Metals, screens such as cathode ray tubes (CRTs) and liquid crystal displays (LCDs), and metal–plastic mixtures account for approximately 60, 12, and 5% (77% total) of the material fractions in e-waste, respectively [1]. Typical e-wastes such as CRT and circuit boards contain As, Cd, Cu, Pb, and Zn [2]. Studies at e-waste recycling sites in Asia have revealed hazardous metal pollution in various environmental media including the air [3,4], soil [4–10], water [10,11], sediments [5,10,12], and dust [6,10,13]. High blood Pb levels in children [14], Pb concentrations in placentas [15], urinary heavy metal levels [16], Cu and Pb in human scalp hair [17], and elevated Pb levels in umbilical cord blood and the meconium of neonates [18] have been identified near e-waste recycling plants, as outlined in a recent review by Chen et al. [3]. Among

environmental media, dust was found to have the highest metal concentration in data from e-waste villages in southeast China [4–6,11–13]. Furthermore, the concentration of Pb in human blood was strongly associated with the Pb concentration in dust [19]. Thus, metals in e-waste dust may seriously impact human health [13]. In addition, not only toxic heavy metals but also precious/rare metals are thought to be released into environmental media. Precious Ag and rare In were detected in soil, air, and human hair from e-waste recycling sites in India [7]. Ag was also detected in soil [10], water [10,11], and sediments [10] at e-waste sites in China and India.

Various e-wastes are exported to the Philippines [20], and many e-waste recycling sites exist around Metro Manila (see Fig. 1 for location of Metro Manila). Many Filipinos prefer to buy secondhand electrical and electronic equipment because of lower price. E-waste is often dismantled and recycled by unregulated companies and untrained individuals in markets or near landfill sites. So, a proper collection system and treatment methods are needed for e-waste in the Philippines [20]. A recent review by Chi et al. [21] divided e-waste recycling into two types: "formal" and "informal". Formal sites are those of an approved company that deals with a large amount of used products from affiliated clients and complies with environmental laws and regulations, such as the factory pictured

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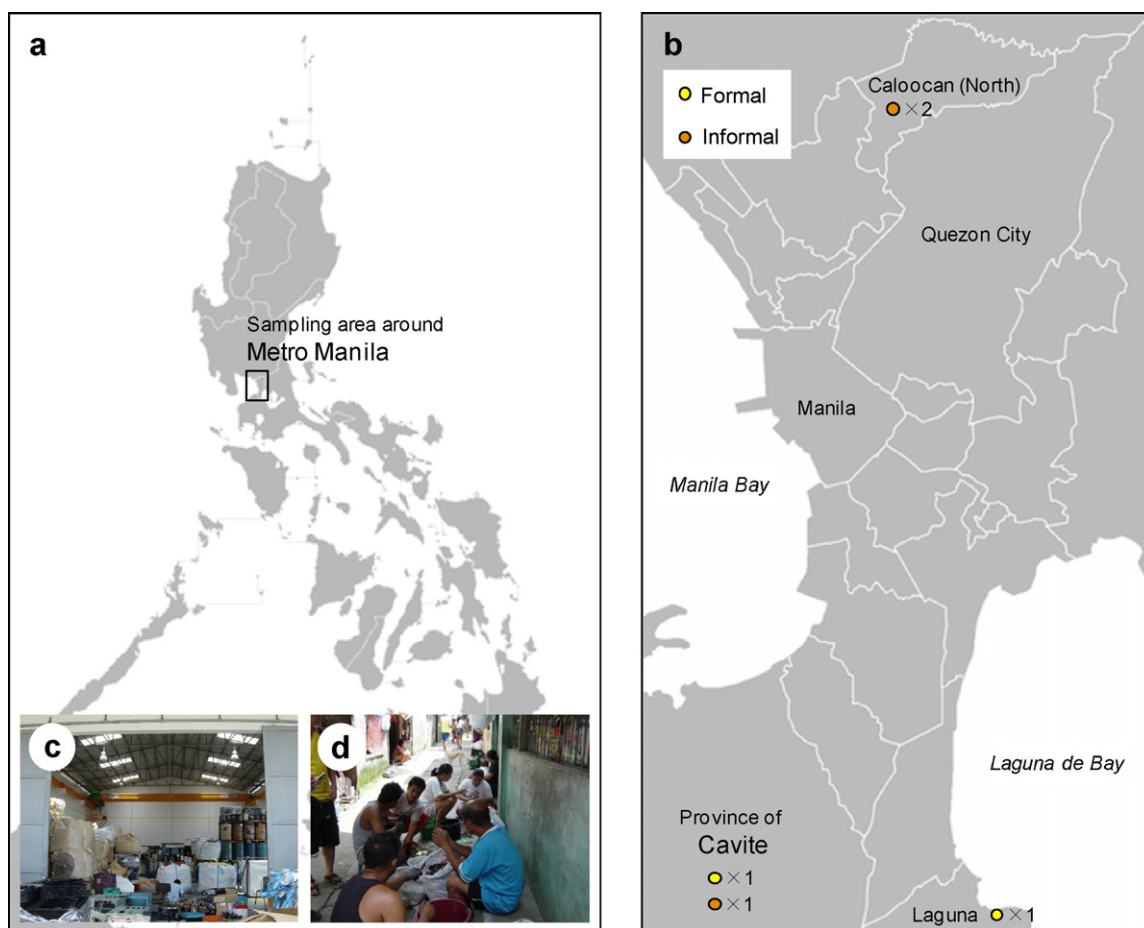
Fig. 1. Sampling area. (a) Overall view of the Philippines. (b) Sampling area around Metro Manila. Formal or informal e-waste recycling sites were visited and soil and dust samples were collected. (c and d) Representative examples of formal and informal sites, respectively.

in Fig. 1c. At the formal sites we visited, employees wore uniforms and, when appropriate, gloves and masks to protect their health. Products at formal sites mainly consisted of plastics, classical e-wastes (e.g., CRTs, refrigerators, circuit boards, wire cables), and recent e-wastes (LCDs, solar panels). In contrast, informal sites are illegal and have a small number of workers, such as the street workers pictured in Fig. 1d. We observed that informal workers rarely protected their hands, mouth, or nose. Informal e-waste is commonly composed of classical waste such as CRTs, circuit boards, and wire cables, etc. We distinguish between the informal and formal sectors based on market size, compliance, working environment, and variety of used goods. Differences between formal and informal sectors may influence which metals are present in environmental media. Previous studies have provided data on surface matrices (soil and dust) at Asian e-waste recycling fields in Guiyu (China, 2003 [5], 2004 [4,13], 2005 [10], 2009 [6]), New Delhi (India, 2005 [10]), Bangalore (India, 2006 [7]), Taizhou (China, 2008 [8]), and Hong Kong (2008 [9]). However, comprehensive intra-Asian comparison had not been reviewed.

In this study, we quantified 11 metals (Ag, As, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, and Zn) in soil and dust surface matrices from formal and informal e-waste recycling sites. We focused on toxic base metals (e.g., Pb, Cu) and precious/rare metals (Ag, In). Soil and dust samples were treated by an acid digestion method [1/1 HNO_3–HCl (v/v), on a hot plate]. Quality control of this digestion method was performed using five certified materials and by comparing our results to those of other studies [13,22,23]. On the basis of comparison with similar datasets from other e-waste sites in Asia [4–10,13], we discuss the current condition of metal contamination in soil and

dust in the Philippines. In addition, we applied an enrichment factor to determine the relative metal concentration in environmental media compared with average crust. We categorized elements in the dust matrix into groups using clustered principal component analysis (PCA). Using these concentration data, a hazard index was calculated to estimate human health risk.

2. Materials and method

2.1. Sampling at formal/informal sectors and preparation

In 2010, we collected soil and dust samples from e-waste recycling sites in northern and southern Metro Manila (Fig. 1a), including Caloocan (North, Metro Manila), Province of Cavite, and Laguna, as shown in Fig. 1b. The terms "formal" and "informal" follow the definitions given in the Introduction. We visited two formal sites in Cavite and Laguna (Fig. 1b and c) and three informal sites in Caloocan (North) and Cavite (Fig. 1b and d). A formal recycling factory was established since 2001. Together informal recycling sites were managed recently. Surface soil (a few cm in depth) was sampled using a shovel within 30 cm area in diameter and manually packed. We excluded foreign fragments such as stone, weed, and waste during sampling of surface soil. Before packing, surface soil was homogenized by a shovel as much as possible. Surface dust was gently swept with a clean broom and sealed in the sample bag. Isolated sweeping areas of dust were selected at each buildings and open-air concrete floors. Table S1 and Supplementary data describe the sampled e-waste recycling sites in detail. After transporting samples to our laboratory, soil and dust samples were

Table 1
Characteristic metal grouping and intra-Asian comparison of four surface matrix types.

	Formal soil	Informal soil	Formal dust	Informal dust
Crust-derived metals	As[b], Cd, Co[a], Fe[b], Mn[a], Ni[c], Pb[c], Zn[c]	As[ab], Co[a], Fe[ab], Mn[a], Ni[c], (In?)	As[a], Co[a], Fe[a], Mn[a]	As[ab], Co[a], Fe[a], Mn[a], (In?)
Enrichment metals	Ag[b], (In?)	Ag[b]	Ag[a], In	Ag[a]
Polluted metals	Cu[c]	Cd[a], Cu[c], Pb[b], Zn[b]	Cd[a], Cu[a], Ni[b], Pb[a], Zn[a]	Cd[a], Cu[b], Ni[b], Pb[ab], Zn[a]
Intra-Asian similarity[*]	Philippines, China, India	Philippines, China, India, Hong Kong	Philippines	Philippines, China, India[**]

Concentrations are ordered by a > b > c according to statistical difference ($p < 0.05$).
"?" means possibility of belonging to each category.

[*] See text for a description of this term.
[**] Without Ag, As, Cd, and Pb from PCBRW, Street B-1, and SSRW in China (ref. Table S8).

air-dried indoors for approximately one week. We then screened the dried soil and dust using 2 and 1 mm mesh screens, followed by powdering the soil and dust using a planetary ball mill (Pulverisette 6, FRITSCH) and freezer mill (6870, SPEX SamplePrep), respectively. Then, soil and dust were sieved to <150 μm for element measurement.

2.2. Measurement of 11 metals and quality control

We used powdered soil and dust samples to measure Ag, As, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, and Zn. Samples (each 1.00 g) were placed in clean conical beakers and digested on a hotplate with HNO_3 (60%, 3 mL) and HCl (35%, 3 mL), i.e., 1/1 HNO_3–HCl (v/v) at 120 °C for approximately 2 h with a watch glass, and 120 °C without a watch glass up to half in liquid (evaporating HCl). After cooling, we filtered the solution with 5B paper (ADVANTEC) and filtrate was used to measure eight metals (Ag, Co, Cu, Fe, Mn, Ni, Pb, and Zn) by inductively coupled plasma-atomic emission spectrometry (ICP-AES; VISTA-PRO, Seiko Instruments) and three metals (As, Cd, and In) by ICP-mass spectrometry (ICP-MS; 7500cx, Agilent Technologies) with a collision gas flow (He) to eliminate interference. We had previously bathed glass and plastic overnight in dilute HNO_3 and rinsed them with Milli-Q water. Five certified reference materials were purchased including powdery solid samples such as soil, sediment, sludge, and dust (Table S2, see Supplementary data). Despite differences in the base matrices, average recovery ratios from the five matrices were satisfactory (including recovery of silver and indium): Ag ($87 \pm 13\%$), As ($84 \pm 11\%$), Cd ($97 \pm 22\%$), Co ($91 \pm 2.8\%$), Cu ($75 \pm 9.3\%$), Fe ($71 \pm 8.7\%$), In (84%), Mn ($78 \pm 11\%$), Ni ($69 \pm 7.4\%$), Pb ($81 \pm 2.2\%$), and Zn ($78 \pm 12\%$).

2.3. Enrichment factor

The enrichment factor (E_f) was defined by the following formula:

$$E_f = \frac{(C/Mn)_{sample}}{(C/Mn)_{crust}} \tag{1}$$

where C is the measured concentration of an element in soil and dust (mg/kg). The enrichment factor represents the level of enrichment compared with average crust [24] ($E_f \sim 1$: same level as average crust). We used Mn as a base material [25,26]. We described detail text in Supplementary data.

2.4. Hazard assessment

We calculated the average daily dose (ADD, mg element/kg weight/day, US EPA Exposure Factors Handbook [27]), hazard quotient (HQ), and hazard index (HI) as follows (ref. detail in Supplementary data):

$$ADD = \frac{C \times IngR \times EF \times ED}{BW \times AT} \tag{2}$$

$$HQ = \frac{ADD}{RfD} \tag{3}$$

$$HI = \sum_i HQ_i (i, \quad element) \tag{4}$$

Oral reference dose (RfD) represents the daily human exposure level that does not pose a risk [28]. When the HQ value is below 1, adverse health effects are unlikely. Here, the HQ value accounts for the toxic risk based on other benchmarks [13,28,29], i.e., ≤1 (minimal), >1–5 (low), >5–10 (moderate), and >10 (high). In this study, we also applied these benchmarks of comprehensive risk assessment to the HI value because the HI value is a summation of the HQ values in Eq. (4).

3. Results and discussion

3.1. Concentration, enrichment, and intra-Asian comparison

We describe and discuss the metal concentrations and enrichment in four types of surface matrices from e-waste recycling sites. We analyze formal soil, informal soil, formal dust, and informal dust around Metro Manila, the Philippines, while referring to soil guidelines (the New Dutch List [30]), as well as previous data from various e-waste sites in Guiyu (China) [4–6,10,13], Taizhou (China) [8], Bangalore (India) [7], New Delhi (India) [10], and Hong Kong [9] (see details of these soils and dusts in Tables S3 and S4, respectively). Statistical procedure is described in Supplementary data. The soil guideline [30] was applied to previous e-waste studies of soil [12] and dust [13] in Asia to determine metal contamination levels. To compare Asian e-waste recycling sites based on previous datasets [4–10,13], we introduce the term "intra-Asian similarity" to indicate similar representative concentration levels of metals in surface matrices between the Philippines and other Asian countries. The term may also be used if representative metal concentrations in surface matrices in other Asian countries are within the concentration range of the Philippines (Table 1). Here, the country refers to the location of the e-waste recycling site.

3.1.1. Formal soil

Fig. 2a shows that formal soil had the lowest metal concentrations of all sample types (Table S5 for details). Formal soil from segmented gardens by e-waste recycling sites had minimal metal pollution, possibly because the surface soil was isolated from the working environment. Concentrations of Cd, As, Co, Ni, Zn, Pb, and Fe in formal soil suggested that there was no enrichment, i.e., geometric mean (GM) E_f values were close to 1, as shown in Fig. 2b (Cd: 2.2, As: 0.87, Co: 1.1, Ni: 0.58, Zn: 1.7, Pb: 2.5, and Fe: 0.64, as described in Table S6). This corresponded to soil levels from our control site, UP (Table S6). Although UP soil was not enriched with Ag ($E_f < 6.0$), Cu (3.5), or In (<5.4), as shown in Table S6, these three metals were enriched approximately 10 fold (median, Fig. 2b) in formal soil. The GM of Cu concentrations was 9.4 (range, 2.6–44) times higher than the optimal soil value [30]. Levels of Ag [7], Cd [7,8], Co [7], Cu [7,8], In [7], Mn [7], Ni [16], Pb [7,8], and Zn [7,8]
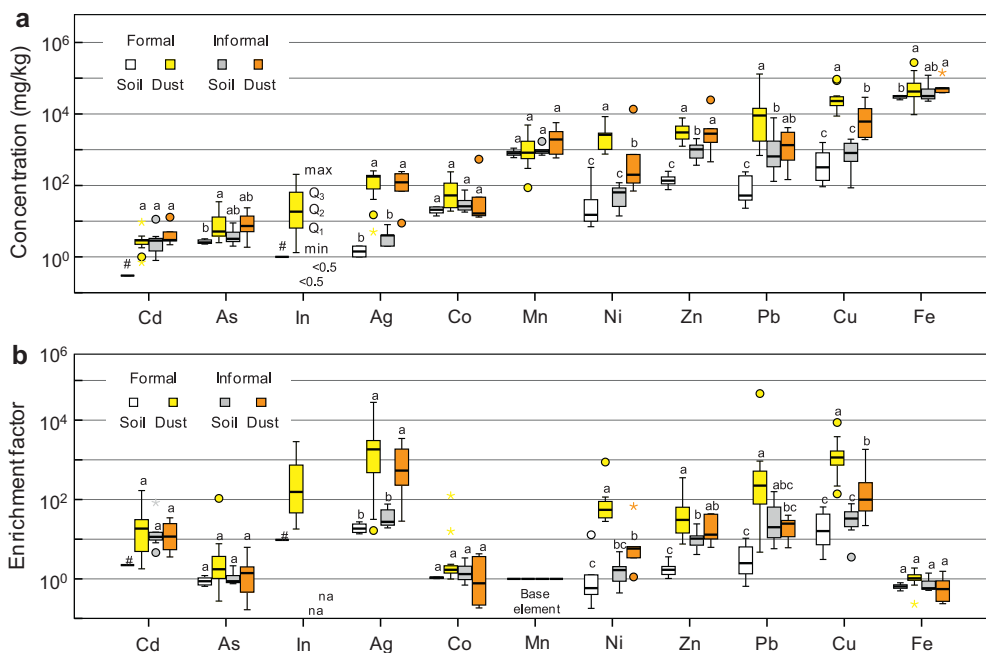
Fig. 2. Box-and-whisker plot of concentration (a) and enrichment factors (b) of 11 elements in soil and dust from formal/informal e-waste recycling. Q_1, Q_2, and Q_3 represent the lower 25% quartile, median, and upper 75% quartile, respectively. Here, interquartile range (IQR) = $Q_3 - Q_1$. Max and min, $Q_3 + 1.5$IQR and $Q_1 - 1.5$IQR, respectively. Circle, mild outlier over the maximum or below the minimum. Asterisk, extreme outlier ($< Q_1 - 3$IQR or $> Q_3 + 3$IQR). (b) Enrichment factors were calculated using $(X/Mn)_{sample}/(X/Mn)_{crust}$ and by referring to crust data [24]. Different letters represent significant differences ($p < 0.05$) in element concentrations between soil and dust based on statistical multiple comparison. The symbol '#' indicates that an element was detected in only one measurement.

were similar in formal-like soils in Taizhou (large-scale e-waste recycling plants A–G [8]) and Bangalore (e-waste recycling facility, BEF [7]), as shown in Table S3. To summarize, Table 1 shows that formal soil (i) had metal content (Cd, As, Co, Mn, Ni, Zn, Pb, and Fe) similar to average natural crust [24], (ii) was enriched in Ag (and possibly In) and polluted with Cu from e-waste recycling sites, and (iii) may have common elemental compositions in the Philippines, China [8], and India [7].

3.1.2. Informal soil

There were no statistical differences in As, Ag, Co, Mn, Ni, Cu, and Fe in informal soil compared with formal soil, as shown in Fig. 2a. Indium was not detected under 0.5 mg/kg anywhere in the informal sites (Fig. 2a). Significantly higher concentrations ($p < 0.05$) of

Pb and Zn (compared to formal soil) suggested that there was specific metal contamination in informal soil from e-waste recycling sites. We confirmed the high E_f values of Cd (GM, 11), Pb (26), and Zn (9.6) in Fig. 2b and Table S6. GM concentrations of Cd, Pb, and Zn were 3.1 (range, 1.0–14), 9.4 (1.5–92), and 6.4 (2.6–14) times higher, respectively, than the optimum soil values [30]. Previous studies of informal soil metals from printer roller dump sites (Guiyu [5]), abandoned workshops (Guiyu [6]), simple household recycling workshops (J–L, Taizhou [8]), e-waste recycling sites in slums (BES, Bangalore [7]), and e-waste dismantling workshops (EW (DW), Hong Kong [9]) are summarized in Table S7. We found similar concentrations of Cd [5–9], Co [7], Cu [5,7–9], Mn [7], Ni [5,8], Pb [5–9], and Zn [6–9] in informal soils among Asian countries. In addition, Pb and Zn concentrations were similar to levels
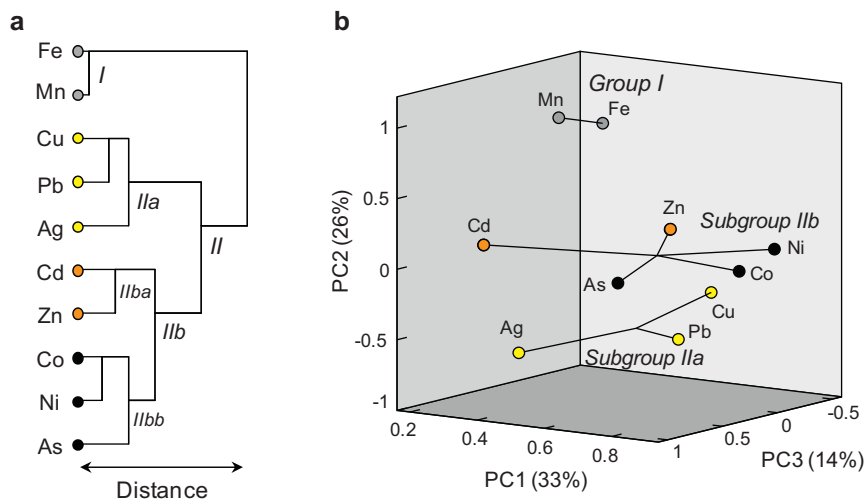

Fig. 3. (a) Hierarchical cluster analysis using the Ward method of 10 elements in formal and informal dust. (b) Principal component analysis of 10 elements in dust shown as a clustered three-dimensional scatter plot. Indium was not analyzed because it was not commonly detected (see Table S2).

in open-burning-site soil at e-waste sites in Guiyu (OBS [4] and S5 [6]) and Hong Kong (EW (OBS) [9]), as shown in Table S3. Soil in an abandoned workshop that had used acid extraction (Guiyu [6]) had As, Cu, and Ni concentrations that were higher than the maximum concentration in informal soil found in this study (Table S7). Since no acid-extraction site existed at the informal sites in this study (see Table S1), differences in recycling activity may have influenced the metal pollutants. Therefore, when including informal soil from e-waste recycling activities such as dismantling and dumpling, we observed the following: (i) As, Co, Mn, Ni, and Fe were crust-like components in informal soil; (ii) enriched metal (Ag) and polluted metals (Cd, Cu, Pb, and Zn) were identified; and (iii) concentrations of specific metals (Cd, Co, Cu, Mn. Ni, Pb, and Zn) had intra-Asian similarity at informal sites in the Philippines, China [5,6,8], India [7], and Hong Kong [9] (Table 1).

3.1.3. Formal dust

Among the four matrix types, formal dust had the highest concentrations of As, In, Ag, Ni, Zn, Pb, Cu, and Fe, as shown in Fig. 2a. Cd concentrations were similar in informal soil/dust. Fig. 2a shows that Ni and Cu had the highest concentrations with GM = 2100 (range, 760–8400) mg/kg and 26,000 (8700–94,000) mg/kg, respectively (Table S5), and were significantly higher than informal dust ($p < 0.05$). The Ag concentrations averaged 95 (range 5.0–250) mg/kg, whereas Pb was 6200 (690–130,000) mg/kg and Zn was 3000 (1300–7700) mg/kg. Metal concentrations in formal dust were statistically similar to informal dust, but higher than formal/informal soils (Fig. 2a). A total of seven formal-dust samples (total $n = 11$) had In concentrations over the detection limit (see Table S5), which suggests that In is a specific rare metal found in formal dust in the Philippines. Formal dust was seriously polluted by Ni, Cu, Pb, and Zn at concentrations 10 (3.6–40), 137 (46–495), 12 (1.3–245), and 4.2 (1.8–11) fold higher, respectively, than in soil action values [30], as shown in Table S3. We confirmed quite high enrichment of Ag, Cu, In, and Pb in formal dust, as indicated by the GM E_f values of 1000, 1100, 190, and 220, respectively (see Table S6 and Fig. 2b). Although As and Fe in formal dust had statistically higher concentrations than in formal soil (Fig. 2a), there was no significant difference in E_f values among the matrices (Fig. 2b). The As and Fe in formal dust may be primarily derived from average crust-like soils, similar to Co and Mn. Here, we could not compare intra-Asian levels of formal dust since no comparable datasets were available. We found that formal dust was a mixture of (i) serious pollutant metals (Ni, Cu, Pb, and Zn) and Cd (polluted modestly), (ii) quite high enrichment metals (Ag and In), and (iii) crust-derived metals (As, Co, Fe, and Mn), as shown in Table 1.

3.1.4. Informal dust

Metal concentrations (excluding In, Ni, and Cu) in informal dust were statistically similar to those in formal dust, as shown in Fig. 2a. Thus, characteristic metal components were similar in informal and formal dust (Table 1). Pb and Zn were the most common pollutants of informal dust and were present at the highest concentrations. We detected no In concentration over 0.5 mg/kg in informal dust. Informal dust had lower concentrations of Ni (GM, 380 mg/kg) and Cu (6300) than formal dust, but higher concentrations than in formal/informal soils (Table S5, Fig. 2a), and 1.8 and 33 times higher soil action values [30], respectively (Table S3). We compared metal concentrations in dust from our sites with concentrations from informal sites having similar activities. These sites included a printed circuit board recycling workshop (PCBRW [8]), streets lined with PCBRWs on both sides (Street B-1 [13]), a separation/solder recovery workshop (SSRW [10]), and a printer dismantling workshop (PDW [10]) in Guiyu, and a circuit board/component separation workshop (CCSW [10]) and a narrow

street recycling workshop (Street N [10]) in New Delhi (picked data up from Table S4). As shown in summarized Table S8, GM concentrations of most metals (Ag, As, Cd, Co, Cu, Mn, Ni, Pb, and Zn) in our informal dust were higher than those in Street N [10] (New Delhi), which is attributable to the dust in Street N being a mixture of dust and soil [10]. The concentration ranges of Co, Cu, Ni, and Zn at our sites included the mean or GM values from every informal site in Guiyu (PCBRW [13], Street B-1 [13], SSRW [10], and PDW [10]) and one informal site in New Delhi (CCSW [10] without Cu), as shown in Table S8. Informal dust around Metro Manila contained Ag, As, Cd, and Pb levels that were similar to those for PDW [10] (Guiyu) and CCSW [10] (New Delhi), but lower than SSRW [10] (China). In addition, the maximum values of Cd (13 mg/kg) and Pb (4100) at the informal sites were below the mean values from PCBRW [13] and Street B-1 [13] in Guiyu (Table S8). Excluding Ag, As, Cd, and Pb in Chinese informal sites (such as PCBRW, Street B-1, and SSRW), Table 1 shows that metal concentrations in informal dust (without soil contamination) may have intra-Asian similarity between the Philippines, China [10,13], and India [10].

3.2. Grouping of metals in dust

During our sampling, dust was generally trapped in a relative closed working space and may reflect e-waste recycling activity. Metal concentrations in dust were similar between formal and informal sites, whereas metal concentrations in soil were not (Table 1). Statistical grouping (clustered PCA) was used to objectively examine Table 1 and the hierarchical metal concentration information in total dust (formal and informal), including its derivation. Square Euclidian distances of standardized logarithmic metal concentrations (Z scores) in total dust samples ($n = 17$) generated a clustering dendrogram based on the Ward method, as shown in Fig. 3a. The greatest distance between two clusters represented the two most different groups: I (Fe and Mn) and II (Cu, Pb, Ag, Cd, Zn, Co, Ni, and As). Group I contained Fe and Mn, which are crust-derived metals, as discussed above (Table 1). Fig. 3a shows that group II was divided into two subgroups: IIa (Cu, Pb, and Ag) and IIb (Cd, Zn, Co, Ni, and As). Subgroup IIa had increased levels of polluted or enriched metals in dust, as also described above (Table 1). We plotted component scores in Fig. 3b, according to PCA results from the correlation matrix of metal concentrations in total dust. Principal components 1, 2, and 3 (PC1, PC2, and PC3, respectively) explained 33%, 26%, and 14% (total of 73%) of the original dataset, respectively. PC1 showed group II (Zn, Ni, Co, As, Cu, and Pb) as high-score metals, as shown in Table S9. Thus, PC1 might be interpreted as the "impact of metal pollution". Crust-derived group I had the highest plus PC2 scores. In contrast, metals at high polluted levels (subgroup IIa) had the lowest negative PC2 score (Table S9). The PC2 axis was interpreted as the "derivation-of-crust indicator" (positive, crust; negative, no crust). Fig. 3b shows that Ag in subgroup IIa was plotted at the lowest (PC1, PC2) coordinate (Table S9), which translates that Ag was not a pollution metal and not derived from crust. This Ag condition is thought to be an "enrichment," supporting its categorization as an "enrichment metal" in Table 1. Based on In concentrations in formal dust ($n = 7$, Table S5), we calculated Pearson's correlations between In and other metals. Logarithmic concentrations of In vs. Cu and Ag indicated higher positive correlations; $r = 0.62$ ($p = 0.14$) and 0.55 ($p = 0.20$), respectively, than In concentrations compared to other metals ($r < 0.5$, $p > 0.2$). However, a larger dataset is required to determine the statistical significance of the differences between the regression coefficients. This implies that In also belongs in the polluted or enriched subgroup IIa (Cu, Ag, and Pb), but only for formal dust. PC2 scores of subgroup IIb existed between group I and subgroup IIa (Fig. 3b). We assumed that subgroup IIb was in a matrix between crust and non-crust, such as a soil/dust mixture. We could statistically separate subgroup IIb into

two sub-subgroups, IIba (Zn and Cd) and IIbb (Ni, Co, and As), as shown in Fig. 3a. PC3 was interpreted as a "Cd-pollution indicator" since Cd had the highest PC3 score (Table S9). High PC1 and PC3 scores of sub-subgroup IIba (as shown in Table S9) are consistent with the Zn and Cd dust pollution levels (Table 1). Although the highest PC1 score of Ni in sub-subgroup IIbb (Table S9) statistically explains Ni pollution in dust (Table 1), similar high PC1 scores of Co and As conflict with their categorization as crust-derived metals based on the E_f values in Fig. 2b (refer to Table 1). However, we concluded that our statistical interpretation of the metal concentrations in dust was accurate.

3.3. Hazard assessment of metals in surface matrices

We calculated hazard indicators (HQ and HI) of metals using Eqs. (3) and (4) to assess noncancer toxic risk and to compare our results with a previous assessment under similar ingestion scenarios of surface matrices from e-waste recycling sites [13]. Through this process, "potential" hazardous risks of surface matrices could be discussed. Slightly polluted by Cu (Table 1), formal soil was thought to pose the lowest risk for adults and children because it had the lowest HI values (median and max <1.0), as shown in Fig. 4a. In contrast, formal dust had significantly higher HI values than the other matrices ($p < 0.005$), excluding informal dust ($p = 0.059$, almost significant difference), as shown in Fig. 4a. Median HI values of formal dust for adults and children were calculated as 4.6 (moderate) and 37 (3.7-fold higher than the 'high' risk), respectively (Fig. 4a, ref. Table S10). Maximum HI values of formal dust indicated that there is an extremely high risk (61 in adults and 490 in children in Fig. 4a). Comparable HI value calculated from summation HQs of Cd, Co, Cu, Ni, Pb, and Zn in formal dust was similar to dust from Street B-1 lined with PCBRWs in Guiyu, China [13] as shown in Table 2. HQ values of Co, Ni and Zn in formal dust were similar to dust from PCBRW [13] (Table 2). Although average HQ_{Pb} in formal dust was lower than in dust from PCBRW [13], on average HQ_{Cu} was approximately 4.0 and 5.3 times higher than that of PCBRW and Street B-1 [13], respectively (Table 2). Thus, Cu might be a specific metal toxin in formal dust in the Philippines. Fig. 4b indicates that Pb and Cu were the main contributors to HI values at 75% and 17% (total 92%), respectively. Formal dust was enriched with In, but the oral RfD of In was not identified in this study. Indium is used in flat panel displays and solar panels as a transparent conductive film (indium-tin oxide, ITO). Some semiconductors also contain InAs or InP. Recent studies have found that ITO [31,32] exposure is associated with lung disease and that InAs [33] or InP [34] may be carcinogenic. In addition, In was detected in the hair of an Indian recycler [7]. These observations suggest health risks from ingesting In compounds from formal dust derived from fragments of high-tech e-waste.
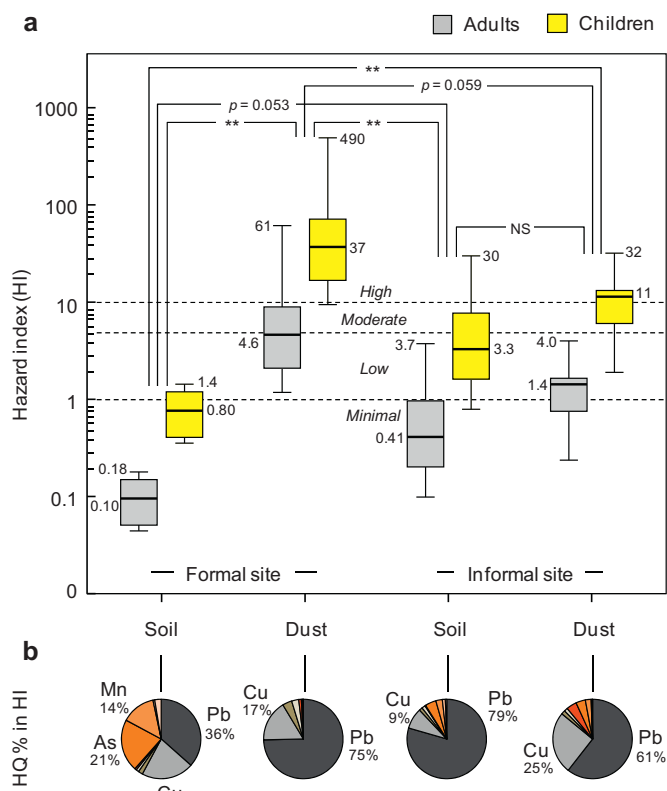
Fig. 4. (a) Hazard index (HI) of adults and children. Summed hazard quotients (HQs) of nine elements (Ag, As, Cd, Co, Cu, Mn, Ni, Pb, and Zn) based on an ingestion scenario from the US EPA exposure factors handbook [27] with an oral reference dose (RfD) [28,36]. Double asterisks (**) represent significant differences ($p < 0.005$). Median and maximum HI values were inserted. NS, not significant. (b) Pie chart describing the ratios of elemental HQs contributing to HI.

There was no difference in the HI values between informal dust and soil (Fig. 4a and Table S10), which was mainly attributed to HQ_{Pb}, as shown in Fig. 4b. However, the HI values between informal dust and formal soil were significantly different ($p < 0.005$). Compared with formal soil, the HI value of informal soil was almost significantly different ($p = 0.053$), as shown in Fig. 4a. Although HI values had no statistical differences in informal surface matrices, Table S10 shows that the median HQ_{Cu} of informal dust was 8.1 times higher than that of informal soil ($p < 0.005$). HQ_{Cu} contributed the most to the HI value in informal dust (25%) among all the matrices (Fig. 4b). Table 2 shows that average informal-dust HQ values of Co, Cu, Ni, and Zn were similar to the PCBRW values in China

Table 2
Children's hazard index (HI) and hazard quotients (HQs) of this study and another comparable study in China [13]. HIs are calculated by summation HQs of Cd, Co, Cu, Ni, Pb, and Zn under the same exposure scenarios and are thus comparable. Bold value ≥1.0. Adults data in Table S11.

City, country	Area, matrix	Average HQs						HI = ΣHQs (Cd, Co, Cu, Ni, Pb, Zn)	
		Cd	Co	Cu	Ni	Pb	Zn	Average	Max
Around Manila, Philippines, this study	Formal sites, soil	0.0038	0.28	0.16	0.011	0.39	0.0054	0.58	**1.22**
	Formal sites, dust	0.013	0.17	**10.7**	**1.78**	**74.3**	0.15	**87.0**	**488**
	Informal sites, soil	0.039	0.047	0.31	0.039	**7.57**	0.045	**8.03**	**29.3**
	Informal sites, dust	0.044	0.35	**3.2**	**1.59**	**6.44**	0.26	**11.6**	**29.8**
Guiyu, China [13]	PCBRW, dust	0.34	0.014	**2.67**	0.96	**402**	0.19	**406**	**772**
	Street B-1, dust	0.18	0.012	**1.97**	0.19	**82.6**	0.10	**85.2**	**502**
	Street B-2, dust	0.072	0.0046	0.23	0.057	**3.60**	0.023	**4.05**	**9.61**
	School yard, dust	0.069	0.0041	0.15	0.032	**2.31**	0.028	**2.75**	**4.32**
	Street L, dust	0.097	0.0072	0.52	0.065	0.83	0.020	**1.82**	**6.73**
	Street G, dust	0.054	0.0027	0.019	0.016	0.25	0.023	0.42	**1.93**
	SU, dust	0.061	0.0057	0.013	0.012	0.22	0.0083	0.40	0.70

[13]. However, informal dust showed lower average HQ$_{Cd}$ and HQ$_{Pb}$ values than PCBRW and Street B-1 [13] (Table 2). Here, we stress the high potential health risk to children by dust (median HI > 10, max 32) or soil (median HI = 3.3, max 30) ingestion from informal e-waste recycling sites (Fig. 4a, ref. Table S10). Children had higher ADD than adults because of the increased ingestion rate and low body weight, calculated conservatively by Eq. (2). At informal e-waste recycling sites, children also worked with their parents or by themselves to survive. Previous studies found that the blood of e-waste workers' children was polluted by lead [14] and their homes showed higher metal concentrations than control houses [10]. Moreover, there was a possibility of heavy metal pollution from mother to baby during childbirth near e-waste recycling sites [18].

4. Conclusions

In this study, we quantified 11 metals (Ag, As, Cd, Co, Cu, Fe, In, Mn, Ni, Pb, and Zn) in soil and dust surface matrices from formal and informal e-waste recycling sites around Metro Manila, the Philippines. We found that surface dust from e-waste recycling sites had statistical higher levels of metal contamination compared to surface soil. In addition, formal and informal sites had different metal contaminations. Our comparison of e-waste recycling sites at the Philippines, China, India, and Hong Kong revealed some similar metal concentrations in surface matrices among geographically distant e-waste sites. This comprehensive intra-Asian comparison provided common insight on metal contamination from e-waste recycling. However, metal concentrations in formal dust were not compared. So, we will need to study on formal dust at other countries in the feature. And, our statistical interpretation (clustered PCA) of the metal concentrations in total dust (formal and informal) was almost accurate and suggested three principal components such as the "impact of metal pollution" (PC1), "derivation-of-crust indicator" (PC2), and "Cd-pollution indicator" (PC3). Especially, subgroup IIa (Cu, Pb, Ag, and maybe In) was interpreted as higher levels of polluted or enriched metals in total dust. Compared with open-air informal sites, the formal sector tended to accumulate metals in indoor surface dust without any natural dilution effect (rain, wind, soil mixture) and had high concentrations of specific metals (e.g., Pb, Cu, Ni, and In). Recently, efforts have been made to divert more e-waste into the controlled formal recycling sector [21]. Although protections such as uniforms, masks, gloves, and eye coverings are adopted in the formal sector (i.e., practical ADD in Eq. (2) might be lower), more rigorous measures may be needed to protect workers against the most hazardous toxic metals (especially Pb and Cu) in formal dust. In contrast, there is also a high health risk for children ingesting surface matrices (dust and soil) from informal e-waste recycling sites. In this study, we compared and assessed the noncancer toxic risk by oral digestion of surface matrices. Further studies are required regarding the contribution of food and water to the ADD, the bioaccessibility/bioavailability of metals [23,35], and toxicological effect using a multi-element matrix.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2012.04.019.

References

[1] R. Widmer, H. Oswald-Krapf, D. Sinha-Khetriwal, M. Schnellmann, H. Boni, Global perspectives on e-waste, Environ. Impact Assess. Rev. 25 (2005) 436–458.

[2] Y.-C. Jang, T.G. Townsend, Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates, Environ. Sci. Technol. 37 (2003) 4778–4784.

[3] A. Chen, K.N. Dietrich, X. Huo, S.-M. Ho, Developmental neurotoxicants in e-waste: an emerging health concern, Environ. Health Perspect. 119 (2011) 431–438.

[4] M.H. Wong, S.C. Wu, W.J. Deng, X.Z. Yu, Q. Luo, A.O.W. Leung, C.S.C. Wong, W.J. Luksemburg, A.S. Wong, Export of toxic chemicals – a review of the case of uncontrolled electronic-waste recycling, Environ. Pollut. 19 (2007) 131–140.

[5] A. Leung, Z.W. Cai, M.H. Wong, Environmental contamination from electronic waste recycling at Guiyu, southeast China, J. Mater. Cycles Waste Manage. 8 (2006) 21–33.

[6] J. Li, H. Duan, P. Shi, Heavy metal contamination of surface soil in electronic waste dismantling area: site investigation and source-apportionment analysis, Waste Manage. Res. 29 (2011) 727–738.

[7] N.N. Ha, T. Agusa, K. Ramu, N.P.C. Tu, S. Murata, K.A. Bulbule, P. Parthasaraty, S. Takahashi, A. Subramanian, S. Tanabe, Contamination by trace elements at e-waste recycling sites in Bangalore, India, Chemosphere 76 (2009) 9–15.

[8] X. Tang, C. Shen, D. Shi, S.A. Cheema, M.I. Khan, C. Zhang, Y. Chen, Heavy metal and persistent organic compound contamination in soil from Wenling: an emerging e-waste recycling city in Taizhou area, China, J. Hazard. Mater. 173 (2010) 653–660.

[9] B.N. Lopez, Y.B. Man, Y.G. Zhao, J.S. Zheng, A.O.W. Leung, J. Yao, M.H. Wong, Major pollutants in soils of abandoned agricultural land contaminated by e-waste activities in Hong Kong, Arch. Environ. Contam. Toxicol. 61 (2011) 101–114.

[10] K. Brigden, I. Labunska, D. Santillo, M. Allsopp, Recycling of electronic wastes in China and India: workplace and environmental contamination, Technical Note 09/2005 (Section 1), Greenpeace International, Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter: Exeter EX4 4PS, UK, 2005.

[11] C.S.C. Wong, N. Duzgoren-Aydin, A. Aydin, M.H. Wong, Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China, Environ. Pollut. 148 (2007) 62–72.

[12] C.S.C. Wong, S.C. Wu, N.S. Duzgoren-Aydin, A. Aydin, M.H. Wong, Trace metal contamination of sediments in an e-waste processing village in China, Environ. Pollut. 145 (2007) 434–442.

[13] A.O.W. Leung, N.S. Duzgoren-Aydin, K.C. Cheung, M.H. Wong, Heavy metals concentrations of surface dust from e-waste recycling and its human health implications in Southeast China, Environ. Sci. Technol. 42 (2008) 2674–2680.

[14] X. Huo, L. Peng, X. Xu, L. Zheng, B. Qiu, Z. Qi, B. Zhang, D. Han, Z. Piao, Elevated blood lead levels of children in Guiyu, an electronic waste recycling town in China, Environ. Health Perspect. 115 (2007) 1113–1117.

[15] Y. Guo, X. Huo, Y. Li, K. Wu, J. Liu, J. Huang, G. Zheng, Q. Xiao, H. Yang, Y. Wang, A. Chen, X. Xu, Monitoring of lead, cadmium, chromium and nickel in placenta from an e-waste recycling town in China, Sci. Total Environ. 408 (2010) 3113–3117.

[16] H. Wang, M. Han, S. Yang, Y. Chen, Q. Liu, S. Ke, Urinary heavy metal levels and relevant factors among people exposed to e-waste dismantling, Environ. Int. 37 (2011) 80–85.

[17] T. Wang, J. Fu, Y. Wang, C. Liao, Y. Tao, G. Jiang, Use of scalp hair as indicator of human exposure to heavy metals in an electronic waste recycling area, Environ. Pollut. 157 (2009) 2445–2451.

[18] Y. Li, X. Xu, K. Wu, G. Chen, J. Liu, S. Chen, C. Gu, B. Zhang, L. Zheng, M. Zheng, X. Huo, Monitoring of lead load and its effect on neonatal behavioral neurological assessment scores in Guiyu, an electronic waste recycling town in China, J. Environ. Monit. 10 (2008) 1233–1238.

[19] B.P. Lanphear, K.J. Roghmann, Pathways of lead exposure in urban children, Environ. Res. 74 (1997) 67–73.

[20] A. Yoshida, A. Terazono, Reuse of secondhand TVs exported from Japan to the Philippines, Waste Manage. 30 (2010) 1063–1072.

[21] X. Chi, M. Streicher-Porte, M.Y.L. Wang, M.A. Reuter, Informal electronic waste recycling: a sector review with special focus on China, Waste Manage. 31 (2011) 731–742.

[22] M. Chen, L.Q. Ma, Comparison of three aqua regia digestion methods for twenty Florida soils, Soil Sci. Soc. Am. J. 65 (2001) 491–499.

[23] A. Turner, K.-H. Ip, Bioaccessibility of metals in dust from the indoor environment: application of a physiologically based extraction test, Environ. Sci. Technol. 41 (2007) 7851–7856.

[24] K.H. Wedepohl, The composition of the continental crust, Geochim. Cosmochim. Acta 59 (1995) 1217–1232.

[25] M. Sakata, K. Asakura, Atmospheric dry deposition of trace elements at a site on Asian-continent side of Japan, Atmos. Environ. 45 (2011) 1075–1083.

[26] W.-H. Liu, J.-Z. Zhao, Z.Y. Ouyang, L. Soderlund, G.-H. Liu, Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China, Environ. Int. 31 (2005) 805–812.

[27] U.S. EPA. Exposure Factors Handbook, Office of Research and Development, Washington, DC, 1997.

[28] U.S. EPA. Integrated Risk Information System (IRIS), http://www.epa.gov/iris/, Sep, 2011.

[29] ATSDR. Public Health Assessment & Health Consultations, Johnstown City Landfill, Johnstown, Fulton Country, New York, 1995, http://www.atsdr.cdc.gov/hac/pha/pha.asp?docid=221&pg=0, Sep, 2011.

[30] VROM, The New Dutch List, Intervention values and target values: soil quality standards, Netherlands Ministry of Housing, Spatial Planning and Environment, Department of Soil Protection, The Hague, Netherlands, 2001.

[31] T. Homma, T. Ueno, K. Sekizawa, A. Tanaka, M. Hirata, Interstitial pneumonia developed in a worker dealing with particles containing indium-tin oxide, J. Occup. Health 45 (2003) 137–139.

[32] D. Lison, J. Laloy, I. Corazzari, J. Muller, V. Rabolli, N. Panin, F. Huaux, I. Fenoglio, B. Fubini, Sintered indium-tin-oxide (ITO) particles: a new pneumotoxic entity, Toxicol. Sci. 108 (2009) 472–481.

[33] M. Van Hulle, K. De Cremer, R. Vanholder, R. Cornelis, In vivo distribution and fractionation of indium in rats after subcutaneous and oral administration of [^{114m}In]InAs, J. Environ. Monit. 7 (2005) 365–370.

[34] P.J. Kirby, C.J. Shines, G.J. Taylor, R.W. Bousquet, H.C. Price, J.I. Everitt, D.L. Morgan, Pleural effects of indium phosphide in B6C3F1 mice: nonfibrous particulate induced pleural fibrosis, Exp. Lung Res. 35 (2009) 858–882.

[35] A.G. Oomen, A. Hack, M. Minekus, E. Zeijdner, C. Cornelis, G. Schoeters, W. Verstraete, T. Van de Wiele, J. Wragg, C.J.M. Rompelberg, A.J.A.M. Sips, J.H. Van Wijnen, Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants, Environ. Sci. Technol. 36 (2002) 3326–3334.

[36] JECFA, Evaluation of certain food additives and contaminants: 41st report of the Joint FAO/WHO Expert Committee on Food Additives, Technical Reports Series No. 837, World Health Organization, Geneva, 1993.